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Thermoelectric properties of $Sm_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.8$) and $Ho_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) perovskite-type oxides

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Recently, we have reported on crystal structure, magnetism, and thermoelectric properties of $Nd_{1-x}Sr_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) [1,2]. These polycrystalline samples exhibit a single-phase perovskite-type crystal structure (space group: *Pnma*). Assuming that the Fe site is in the mixed-valence stat, the spin state of Fe changes from a low-spin (LS) or intermediate-spin (IS) Fe^{3+} ions dominant state at $x \leq 0.5$ to a LS Fe^{4+} ions dominant state at $x \geq 0.6$. Using the high-temperature limit equation which is an extension of the Heikes formula for Seebeck coefficient for iron oxides, the thermoelectric characteristics tend to be p-type when Fe^{3+} and Fe^{4+} ions are predominantly LS at $x \leq 0.5$, whereas they tend to be n-type when Fe^{3+} and Fe^{4+} ions are predominantly IS and LS at $x \geq 0.6$, respectively. In fact, at temperatures less than 500K, these samples show a p-type Seebeck coefficient for $0.1 \leq x \leq 0.5$ and an n-type Seebeck coefficient for $0.6 \leq x \leq 0.9$. However, for $0.6 \leq x \leq 0.9$, a part of Fe^{4+} ions is reduced to Fe^{3+} ions because of an oxygen deficiency in the 500 - 600K temperature range, whereas compositions with high n-type *ZT* could not be identified.

Polycrystalline $Sm_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.8$) and $Ho_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) samples were synthesized using a general solid-state reaction method. The oxygen deficiency δ was determined from the average value obtained from three iodometric titrations. All the samples were subjected to powder X-ray diffraction measurements by using SmartLab (Rigaku), and the crystal structures were identified using Rietveld analysis by the RIETAN-FP program. ResiTest8300 (TOYO) was used for electrical resistivity and Seebeck coefficient measurements from 80 to 395 K, and a home-made apparatus was used for measurements from 395 to 600 K. Thermal conductivity measurements from 300 to 800 K were used by PEM-2 (ADVANCE RIKO), and *ZT* up to 600 K was evaluated.

From crystal structure analysis, all samples exhibit a single-phase perovskite-type crystal structure (space group: *Pnma*). As with $Nd_{1-x}Sr_xFeO_{3-\delta}$ for $x \geq 0.6$ [1,2], it was found that a part of Fe^{4+} ions in $Sm_{1-x}Ca_xFeO_{3-\delta}$ for $x \geq 0.6$ is reduced to Fe^{3+} ions because of an oxygen deficiency in the 500 – 600K temperature range, and high n-type thermoelectric properties could not be identified. On the other hand, $Ho_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) samples show a magnetic susceptibility about 200 times higher than that of $Sm_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) at 5 K. This suggests that all of the Fe ions in $Ho_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) samples are in the high-spin (HS) state, i.e., HS $Fe^{3+}{}_{1-x}$ HS $Fe^{4+}{}_x$, rather than (LS Fe^{3+}, IS Fe^{3+})$_{1-x}$ LS $Fe^{4+}{}_x$. In fact, the temperature dependence of the reciprocal magnetic susceptibility above 700 K confirmed that the Fe in $Ho_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) samples is in the HS state. Therefore, $Ho_{1-x}Ca_xFeO_{3-\delta}$ ($0.1 \leq x \leq 0.9$) samples are expected to exhibit both high p-type and n-type thermoelectric properties at high temperature.

References

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[2] Nakatsugawa, H., Kamatani, Y., Okamoto, Y., Hervoches, C.H., *Jpn. J. Appl. Phys.* **2023**, *62*, 069401.